A REPORT ON THE LABORATORY EVALUATION OF FIVE CHEMICAL ADDITIVES USED FOR THE REMOVAL OF OIL SLICKS ON WATER

DIVISION OF RESEARCH

ONTARIO WATER RESOURCES COMMISSION

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NOTICE

All chemical products mentioned in this report were examined and tested under laboratory conditions to obtain some pertinent data from which to ascertain the general suitability and the effectiveness of such chemicals as oil dispersants for combatting oil pollution problems, and to assess their resultant effects on the water quality and aquatic life when used for this purpose.

The selection of these particular chemical products for testing purposes was made simply on their availability at the time of this study. No further studies are being contemplated to carry out similar tests on any or all of the commercial products that may be available for combatting oil pollution problems.

The publication of this report does not, in any way, indicate the approval, endorsement, guarantee, recommendation, or representation of any kind whatsoever by the Commission with regards to the use of these chemicals as oil dispersants. Neither does it imply nor obligate the Commission, its employees or agents, to conduct any similar tests in the future on these products or any other products designated for this purpose.

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SUMMARY

Five chemical additives developed recently as oil dispersants to combat accidental oil spills and remove oil slicks floating on waters were evaluated under laboratory conditions with tests on samples of petroleum crudes and fuel oils. All of these were found to have varying degrees of effectiveness in dispersing and emulsifying samples of oil tested.

Two of these chemicals, Ameroid Oil Spill Emulsifier #1 and Pero-Klean 818 were considered to be the most effective oil dispersants from the standpoint of the amount required to achieve good dispersion with the samples of oils tested. Unfortunately, they were found to be very harmful to fishes at very low concentrations and had a tendency to inhibit biological activity in the activated sludge treatment process. In addition, they contain highly odorous materials which may give rise to undesirable odours in potable water supplies if present in trace quantities.

Corexit 7664 was found to be the least toxic. Bioassay tests revealed that Pimephales promelas (fathead minnows) could survive for a short duration without any difficulty in water containing up to 10,000 ppm while, in

contrast, the other four chemicals were found to be lethal at concentration levels of 10 ppm.

In spite of its non-toxic feature, Corexit 7664 was found to be somewhat less effective in dispersing crude oils than some of the other oil dispersants tested.

Two other chemicals, Jansolv-60 and Polycomplex A-11 were found to be reasonably good in dispersing most of the oils tested but they were also lethal to fishes at concentration levels of 10 ppm.

INTRODUCTION

Since the disaster of the ill-fated Torrey Canyon on March 19, 1967, several chemicals and materials have been developed and introduced on the market to combat floating oil slicks resulting from accidental oil spills and to control subsequent oil pollution problems. The most notable of these consist of chemical oil dispersants and emulsifiers that are capable of forming complexes with the oil. When applied to the oil/water mixtures, they help to disperse or solubilize the oil in water. Many of these products are claimed to be capable of converting oil slicks into tiny microsized particles which will disperse harmlessly in the water. They are said to be non-toxic to aquatic life and readily biodegradable.

At the time of the Torrey Canyon incident, there was very limited information available concerning the physical and chemical properties of the oil and the chemical detergent,* and even less knowledge about their probable biological effects. Extensive investigations conducted by the British scientists

* The word "detergent" as quoted from the literature means a mixture of two or more compounds including a surfactant and an organic solvent and should not be confused with the chemical formulations sold as cleaning agents for household use.

in the aftermath have revealed very forcefully that the detergent chemicals employed in removing and dispersing the oil in the affected areas were found to be more deadly and far more damaging to marine life and ecology than the oil itself. (1) (2) (3)

The purpose of this study was to evaluate some of the chemical additives that are sold as oil dispersants and to compile some pertinent data with regards to their

(a) effectiveness as oil dispersants,

(b) biological treatability,

(c) toxic effects on fresh water fishes and

(d) effects on palatability of water.

CHEMICAL CHARACTERISTICS OF OIL DISPERSANTS

A cursory review of the literature has indicated that many of these oil dispersant chemicals are a mixture of several compounds consisting of a non-ionic surface-active agent (surfactant), an organic solvent and a stabilizer. The non-ionic surfactant may consist of polyethanoxy compounds or polyglycols. These are widely used in the preparation of cleaning agents and detergents formulated for cleaning and removing oily materials and other petroleum derivatives. Solvents usually consist of high aromatics which allow the surfactant to mix with the oil and form an emulsion with water. Stabilizers are added in the formulation to achieve stable emulsions and this, in turn, enhances the dispersion of the oil in water. (3) (4)

Laboratory examination involving infra-red spectroscopic techniques has indicated that all of these oil dispersants contain non-ionic surfactants and each has a different one. Only two of these tested were found to have compounds with nearly similar characteristics.

TEST PROCEDURES

General

Five samples of oil dispersants were examined and evaluated under laboratory conditions. Table 1 gives a list of chemicals tested and the names of their suppliers. Although there are numerous other chemicals sold as oil dispersants, no attempt was made to evaluate all of them.

The evaluation tests were conducted on samples of crudes and fuel oils considered to be representative of those obtainable at oil refineries in Ontario. These are listed in Table 2. The crude oils include those from Alberta, Saskatchewan and three producing fields located in south-western Ontario.

Effectiveness as an Oil Dispersant

Two methods were used to assess the effectiveness of these chemicals as oil dispersants. Basically, they involved the application of the chemical on the oil slick floating on the surface of the water and then followed by agitation.

In one method, the chemical was applied as a fine spray on the oil slick using a spraying device that was activated by a pressurized propellant. The oil was spilled

Table 1

LIST OF OIL DISPERSANTS

Name	Supplier	Approx. Price
Ameroid Oil Spill	Drew Chemical Ltd., Ajax, Ontario.	$3.05 to 3.60/Imp. gal
Corexit 7664	Enjay Chemical Ltd., 1937 Leslie St., Don Mills, Ontario.	$5.60 to 6.00/Imp. gal
Jansolv-60	Sunshine Chemical Corp., Jacksonville, Florida, U. S. A.	not available
Pero-Klean 818	Perolin Co. of Canada Ltd. 1151 Kipling Ave. N., Rexdale, Ontario.	$3.10 to 3.50/Imp. gal
Polycomplex A-11	Shield Chemical Ltd., 17 Jutland Road, Toronto, Ontario.	$4.00 to 5.00/US gal

The prices given are only approximate and they may vary with the quantities purchased. They do not include transportation costs or any other charges.

Table 2

LIST OF OIL SAMPLES USED FOR THESE STUDIES

Sample	Source
Crudes	
Alberta Mixed	Texaco (Canada) Ltd.
Cambrian *	Clearville, Ontario
Devonian *	Rodney, Ontario
Leduc 852	British American Oil Co. Ltd.
Saskatchewan	Texaco (Canada) Ltd.
Silurian *	Mosa Township, Ontario
Western (composite)	Shell Canada Ltd.
Fuel Oils	
Bunker C	British American Oil Co. Ltd.
Diesel Oil	Texaco (Canada) Ltd.
Furnace Oil	Imperial Oil Ltd.

* Ontario crudes were supplied by Imperial Oil Ltd. (Chatham) and Ontario Department of Energy and Resources Management.

on the surface of water placed in a shallow rectangular pan which could be set into motion by means of a mechanical shaking device*. The latter could be easily regulated to move at any desired speed to provide gentle or vigorous movements of water, similar in effect to the natural wave actions produced on lakes or other bodies of open water.

The second method involved the use of a multiple stirrer, a test apparatus employed in jar-test procedures at waterworks plants. A sample of oil consisting of approximately 0.5 to 1.0 percent by volume was placed in a beaker of water and then treated with the undiluted oil dispersant. The latter was applied carefully to the surface of the floating oil slick through a pipette, one drop (0.1 ml) at a time. After each drop, the entire contents of the beaker was agitated with the stirrer for a few minutes and then stopped. About five minutes later, another drop of oil dispersant was applied and then stirred. This process was repeated until all of the oil had been dispersed completely or when a predetermined dosage of oil dispersant had been added.

* Dubnoff Metabolic Shaker

Biological Treatability

The biological treatability of these oil dispersants was determined by techniques similar to those described by Lamb and his associates.(5) This involved the use of a respirometer and a membrane-covered oxygen electrode to measure activity and oxygen utilization rates of an endogenous sludge that had been fed with varying amounts of oil dispersants.

Toxicity Studies

All of the oil dispersants were subjected to toxicity evaluation tests by the routine bioassay method prescribed in the Standard Methods (6) utilizing fathead minnows, *Pimephales promelas*, as test animals.

Threshold Odour Tests

Standard threshold odour tests at 60°C were performed on a series of tap water samples contaminated with 1 ppm of oil dispersant.(6) Similar tests were also conducted on another series of samples contaminated with the oil dispersant but subjected to chlorination. Prior to the odour tests, excess chlorine residual was removed by stoichometric addition of a dechlorinating agent.

No attempt was made to establish the detectable limits or the minimal concentrations at which odours can be

detected. The results obtained from these tests were qualitative and intended to show the effects of these chemicals on the palatability of water when contaminated with 1 ppm and the effect of chlorination.

DISCUSSION OF RESULTS

The results of various laboratory analyses and evaluation tests are summarized in Table 3.

Chemical Dosages

The test data related to Chemical Dosages show the range of dosages of the given oil dispersants that was applied to various samples of crudes and fuel oils in order to obtain a reasonably good dispersion. These are compared to the "Recommended Dosages" as noted in the manufacturer's information bulletins.

Although most of the oil samples (Table 2) responded very well to treatment at the recommended dosage, it was found generally that a much higher dosage of chemicals was needed to effect good emulsification and dispersion particularly in some of the crudes. This will be discussed below.

Dispersing Qualities

In the tests with all the oil samples, spraying was found to be the most effective method of applying oil dispersants on the oil slicks. The dispersing action of the chemical was greatly enhanced and made more effective when its application was followed by vigorous agitation. For this reason the manufacturers of these products insist upon the use of agitation in conjunction with their application.

Not all of the oil dispersants reacted equally well with all the oil samples. The data presented in Table 3 indicate some of the oil samples with which each product was found to be extremely effective and others with which it had only very limited effects. It should be noted that all of these oil samples were dispersed by the chemicals but in many instances, higher dosages were required; reactions were somewhat slower and even with application of higher dosages, the oil slicks could not be completely dispersed.

Toxicity

According to the information given in the technical data sheets and bulletins supplied with each product, all of these oil dispersants are claimed to be biodegradable and non-toxic. When applied to synthetic detergents and surfactants including chemical oil dispersants, the term "biodegradable" is usually taken to mean biological decomposition under aerobic conditions.(7)

There was no attempt to assess the biodegradable aspects of these chemicals but it was decided to evaluate their biological treatability in the activated sludge treatment process; in other words, to determine what effects, if any, they may have on the activated sludge process.

Table 3

SUMMARY OF DATA

	Ameroid Emulsifier #1	Corexit 7664	Jansolv-60	Pero-Klean 818	Polycomplex A-11
Chemical Dosage (1)					
Recommended	1-20	1-10 to 1-20	not given	not given	1-10
Required	1-10 to 1-20	1-2 to 1-5	1-2 to 1-10	1-5 to 1-10	1-5 to 1-10
Most Effective on these oils	All oils except Devonian crude	fuel oils and Cambrian	fuel oils and Silurian	fuel oils Saskatchewan Silurian	fuel oils Cambrian Saskatchewan
Least effective on these oils	Devonian	Leduc	Western Cambrian	Alberta Leduc Cambrian	Western
Toxicity Data					
TL_m value (2)	6.1 ppm	10,000 ppm	9.5 ppm	5.3 ppm	13 ppm
Tolerance Level (Endogenous Sludge)	0.1%	1.0%	1.0%	0.5%	1.0%
Odour Characteristics					
Description	Kerosene	fatty acid	pine oil	moth ball	household detergent
T.O.N. at 1 ppm	> 200	< 2	10	> 200	< 2
Affected by Chlorination?	no	yes	no	yes	no

NOTES: (1) Figures given for Chemical Dosage indicate the ratio of one part of oil dispersant per given number of parts of oil.

(2) TL_m are determined for a 96-hr period for all samples except Corexit 7664. The value given for Corexit 7664 is the threshold toxicity level as determined in the range tests.

The result obtained from these studies are presented in Table 3 under the heading of "Tolerance Level" (Endogenous Sludge) and expressed in terms of percent concentration. This implies that when the given concentration of oil dispersant was fed to the endogenous sludge, some inhibitory effects on the microbial activity was observed as indicated by changes in the depletion rate of dissolved oxygen.

Although the data given for three oil dispersants, namely Corexit 7664, Jansolv-60 and Polycomplex A-11, show one percent as the "Tolerance Level", it is believed that the actual figure may have been slightly higher. There was no attempt made to conduct these tests using chemicals at concentrations over one percent.

Ameroid Oil Spill Emulsifier #1 and Pero-Klean 818 seemed to have some adverse effects on the microbial activity at concentrations of 0.1 and 0.5 percent respectively.

The results of the bioassay studies are expressed as TL_m values. They represent median tolerance limit on the concentration at which 50 percent of the test animals may survive. It is obtained by interpolation of experimental data related to the observed number of test animals surviving at the end of the given time of exposure in the test samples.

According to the test data, Corexit 7664 was the only chemical tested which did not show any toxic effects on the *Pimephales promelas* (fathead minnow) even though they were exposed to very much higher concentrations than with the other chemicals. Other oil dispersants were found to be extremely toxic at very low levels of concentration as indicated by the TL_m values. Most toxic of these were found to be Ameroid Oil Spill Emulsifier #1 and Pero-Klean 818 which had TL_m values of 6.1 ppm and 5.3 ppm respectively.

Taste and Odour Characteristics

All of the oil dispersants had a characteristic odour which was believed to be attributable to the organic solvent in which the surfactant chemical was dissolved. The description of odours and Threshold Odour Numbers (T.O.N.) are given in Table 3.

T.O.N. values indicate the relative odour intensities of the chemical oil dispersants present in tap water at the concentration of 1.0 ppm. These were determined by routine odour tests at 60°C. T.O.N. value is a measure of the odour intensity and represents the number of times that a test sample water must be diluted with odour-free water in order to give the least detectable odour.

Two samples, Ameroid Oil Spill Emulsifier #1 and Pero-Klean 818 were found to impart very intense odours at concentrations of 1.0 ppm with T.O.N. values greater than 200.

The odours emitted by two of the oil dispersants were found to be slightly intensified after chlorination. They were Corexit 7664 and Pero-Klean 818.

CONCLUSIONS

Based on the results of laboratory investigations and the review of technical bulletins supplied with the chemical oil dispersants, the following conclusions are presented:

1. The main active ingredient in most of these oil dispersants is believed to consist of a non-toxic surfactant dissolved in an organic solvent that is capable of emulsifying with water. Another substance, a stabilizer, is usually added to assist in the formation of a stable emulsion.

2. All of the chemicals examined exhibited varying degrees of effectiveness in emulsifying and dispersing samples of oils used in this study. It was generally found that fuel oils, notably Bunker C and other lighter grades, could be dispersed without any difficulty when treated with adequate dosage of oil dispersant.

3. Spraying was found to be the best method of applying oil dispersants on floating oil slicks but for the best results, this should be followed by vigorous agitation.

4. In nearly all of the tests, it was found that only a minimum amount of agitation was needed to keep the oil slick well-dispersed once it had been treated with the chemical and solubilized. However, as soon as the agitation was

discontinued, the dispersed particles of oil had a tendency to rise slowly, conglomerate, and reform into an oil slick on the surface.

5. All of the oil dispersants worked very well with some oil samples when applied at the dosages recommended by the manufacturers but in most cases, it was generally found that slightly higher dosages were required to achieve good dispersion.

6. Ameroid Oil Spill Emulsifier #1 and Pero-Klean 818 were found to be the most effective oil dispersants when used in very low concentrations. However, the other tests indicated that these exhibited toxic effects on fresh water fishes and sewage organisms in activated sludge.

7. Corexit 7664 was the only chemical tested that did not show any adverse effects on fishes at high concentrations whereas the others were found to cause some difficulties at concentrations in excess of 10 ppm.

8. Threshold odour tests indicated that Ameroid Emulsifier #1 and Pero-Klean 818 imparted very strong odours to the water at concentrations of 1.0 ppm.

9. The cost of these oil dispersants are relatively high. If an oil spill involving thousands of gallons of oil occured, the cost of cleanup may be very high.

RECOMMENDATIONS

The use of chemical oil dispersants should not be considered as the most satisfactory method of cleaning up accidental oil spills and combatting oil pollution because of the cost of the dispersants, and their far-reaching effects on the palatability of potable water supplies, fishes and other aquatic life.

If large volumes of oil are involved, attempts should be made to utilize physical methods such as skimming and adsorbent materials to remove the bulk of oil and then use the oil dispersants for eliminating oil slicks floating on water.

For the best results, oil dispersants should be sprayed directly on the oil slick by spraying devices, and then followed by vigorous agitation.

Because of the adverse effects resulting from their use, chemical oil dispersants should be employed with discretion. Their application should be limited to the control and abatement of oil pollution only in emergency situations.

All chemical oil dispersants should not be considered to be universally applicable to the treatment of all oils. Each of the chemical formulations that are available

commercially as oil dispersants should be tested thoroughly with various types of oils in order to obtain some background information.

It is recommended that future studies involve the oil analyses to determine what constituent in the oil, if any, governs the ease with which it will react and disperse with the oil dispersants.

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